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Description

Value document provided with a security element and method for producing said value document

The invention relates to a value document with at least one security element, which comprises in a marker region a marker layer applied to carrier paper and comprising electroluminescent pigments. It further concerns an electroluminescent pigment suitable for use in such a value document, a method for production of such a value document and a method for production of such electroluminescent pigments.

To protect against counterfeiting or imitation, value or security documents such as for example bank notes, identity cards or chip cards are fitted with so-called security features or elements which are to exclude securely, for example in paper value documents amongst others, imitation by the production of colour copies. The security elements can in particular be designed as optically variable elements such as for example holograms or interference layer elements which, depending on the viewing angle, show different print impressions when viewed but are not transferred to the copy in the copying process. Such security elements are however difficult or impossible to read or analyse by machine so that automated security checking of the value document concerned is possible only within limits and with great technical complexity.

DE 197 08 543 discloses however a value document which is particularly suitable also for automatic evaluation of its security element. For this as a security element the value document has applied to the carrier body, for example the bank note paper, in a marker region a marker layer which is mixed with electroluminescent pigments. In checking or authentication of this security element the marker layer containing the electroluminescent pigments is subjected contactless to an electrical alternating field via a correspondingly designed tester.

The electrical alternating field stimulates the electroluminescent pigments contained in the marker layer firstly to emit electromagnetic radiation which can be recorded directly or indirectly in a suitable receiver. In particular in combination with the

corresponding tester the value document equipped in this way is particularly suitable for automatic and hence particularly reliable analysis with only limited technical complexity.

The invention is based on the object of creating a value document of the above type which has a particularly high security standard. Also disclosed are an electroluminescent pigment suitable for use in such a value document, a method for production of such a value document and a method for production of such pigments.

In relation to the value document this object is achieved according to the invention in that the electroluminescent pigments each comprise a pigment core formed of electroluminescent material which is surrounded by an optically active coating.

The invention is based on the consideration that a value document should be equipped with electroluminescent pigments for a particularly high security standard.

In the analysis of radiation emitted by electroluminescent pigments, usually the receiver part of the tester used is tuned to the emission spectrum of the electroluminescent pigments. With targeted use of electroluminescent pigments with mutually distinguishable spectra, it is therefore possible to structure the characteristic signature of the security feature particularly clearly and hence improve the quality of authentication. In the sense of authentication it can be provided, to determine a degree of correlation, to compare a spectrum received during testing with an expected spectrum. This achieves a greater precision in analysis and hence a higher security function of the security feature concerned for the value document, the more specific the setting of the spectrum emitted by the electroluminescent pigments, where a more sharply defined spectrum allows higher selectivity and precision than a broader spectrum. However the emission spectra of known electroluminescent pigments are comparatively broad and can only be extended to a limited number of mutually clearly distinguishable spectra by the addition of more suitable doping.

The value document should be designed for a particularly high security standard with electroluminescent pigments which are designed in particular for the emission of a characteristic, selectively identifiable spectrum. Such a selectively identifiable

spectrum should in particular have a comparatively small bandwidth so that on wavelength-sensitive evaluation a particularly reliable allocation of emitted signals to individual pigment groups or types is possible. Authentication can be made dependent in particular on the presence of specific pigment groups or types. For a comparatively small bandwidth of the emitted spectrum, the electroluminescent pigment core should be coated such that wavelength-dependent, the actual spectrum emitted by the electroluminescent material is partially "filtered". For this the coating is designed as an optically active coating. For example with a monolayer coating a wavelength-selective transmission takes place by use of a non-linear absorbent coating. With such a non-linear absorbent coating, for example by targeted doping of the coating e.g. with metal ions (Fe^{3+}, Co^{3+}, Ni^{3+}), suitable energy levels can be generated in the crystal lattice of the coating which in adequate light intensity can be stimulated and hence achieve the non-linearity. The coating can be designed so that defined parts of the emission spectrum are suppressed.

Particularly advantageous optical properties can suitably be achieved by the targeted use of interference effects by which the spectrum emitted can be suppressed or attenuated in a targeted fashion in individual wavelengths or wavelength ranges. Use of such interference effects is achieved by coating of the electroluminescent pigment cores preferably with at least two layers with different refractive indices.

In principle the coating of pigments with a series of thin layers of varying refractive index is known from EP 1 138 743 A1 or EP 0 852 977 A1. The concepts defined there are however oriented towards a coating of magnetic pigment cores, where the coatings should ensure an increased refractive index and hence high reflectivity and a light colour of the pigment. The methods described in these publications for application of the coatings to the pigment cores can be used also in the present concept.

Advantageously the value document is suitable for application of the security element to the carrier body with a printing method, preferably by screen printing, rotogravure, offset printing, letterset printing or a transfer process. For this the pigments suitably have a mean pigment size of around 1 μm to 50 μm, preferably 3 μm to 8 μm, so they are particularly suitable for use in a security printing process.

Particularly fine-grained pigments are available which are consequently particularly suitable for use in a printing process; here the electroluminescent material forming the pigment core concerned advantageously has a preferably cubic crystal structure.

The electroluminescent material forming the respective pigment core suitably comprises a II-VI compound, advantageously (co)-doped ZnS, ZnSe, SrS, CaS or CdS, where in a further preferred embodiment the doping comprises as an activator Cu and/or Au and/or Mn and as further activator halogenide ions or trivalent cations. Alternative or additional advantageous doping can be Ag, Fe, Co, Ni and/or rare earths such as in particular Tm, Tb, Dy, Gd, Yb, Sm, and Eu.

The coating surrounding the pigment core in the manner of micro-encapsulation preferably has at least one layer of inorganic material preferably oxides, nitrides, oxysulphides, sulphides of metals or semi-metals which where applicable are (co-)doped with metals or semi-metals. In a further advantageous embodiment suitable inorganic materials are SiO_2, SiO, TiO_2, NiO, Ni_2O_3, CoO, Co_2O_3, Y_2O_3 or ZrO_2. In an alternative or additional advantageous embodiment, the inorganic material comprises a metal, preferably Fe and/or Co and/or Ni and/or Cr and/or Mo and/or W and/or V and/or Nb.

Depending on the electrical conductivity of the coating, the encapsulation of the pigment cores by coating in the manner of a Faraday cage could lead to the pigment cores being screened completely from externally applied electrical fields. This would make it difficult or completely impossible to stimulate the pigment core by the electrical field, in particular the electrical alternating field, on authentication of the value document. Thus in a further advantageous embodiment the coating covers the surface of the pigment core only partly.

Advantageously the coating is designed to profile the emission spectrum of the pigment core concerned to a particular extent and modify this for a particular characteristic signature. In order in this sense to provide an emission spectrum of the pigment with comparatively small bandwidth, the coating in a particularly advantageous embodiment is selected with regard to refractive indices of its layers or in its coating thickness such that the spectral transmission of the coating shows a

maximum at a pre-specified wavelength, preferably a wavelength at which the natural emission spectrum of the electroluminescent material is particularly pronounced. The material parameters of refractive index and/or layer thickness are specified in a targeted manner so that the desired focusing of the emission spectrum of the pigments occurs due to the use of the interference effects in the coating. By corresponding pre-specification the coating for example can act in the manner of a band filter or an upper or lower edge filter, and maxima can be shifted or additional maxima generated in the emission spectrum.

With reference to the electroluminescent pigment, the said object is achieved in that a pigment core formed of electroluminescent material is surrounded by a coating with non-linear transmission and/or absorption behaviour. Particularly advantageous refinements of the electroluminescent pigment and coating correspond to the embodiments provided for the value document.

Such an electroluminescent pigment can preferably be used in a luminescent device as a light-emitting component of LED's, displays or background lighting. The coating suitably protects the electroluminescent pigment from environmental influences, in particular against water vapour migration.

To achieve the object concerning the method for production of the value document, two variants are proposed which can be applied individually or in combination. In a first variant, to produce the marker layer a resin is applied to the carrier body and softened, where in the softened state of the resin pigment cores are applied such that the pigment cores sink at least partly into the resin so that only part of the surface of the pigment core protrudes from the resin, where the coating is subsequently applied by means of physical vapour deposition (PVD) and/or chemical vapour deposition (CVD). This ensures that in coating the pigment cores only part of their surface is given the coating so as to exclude securely the screening of the pigment cores from the stimulating electrical field due to a completely enveloping surface coating.

Advantageously an acrylate-based resin is used, where as an alternative or additional advantageous refinement the pigment cores are scattered on the resin by

a sieve. The use of the sieve allows in a particularly simple manner a high homogeneity and even distribution of the pigment cores over the surface.

In a second variant the marker layers are applied to the carrier body by means of a printing process, preferably by means of screen printing, rotogravure, offset printing, letterset printing or transfer printing process. Such a process is suitable in particular for the production of large quantities with comparatively simple means.

Here advantageously in application of the marker layer a printing ink is used which contains a solvent and/or a binding agent in addition to the electroluminescent pigments. Suitably the printing ink with regard to its composition and constituents is designed for a particularly favourable use in a printing process. For this the printing ink advantageously contains a pigment proportion of less than 30%, advantageously less than 25%.

With regard to the method for production of electroluminescent pigments particularly suitable for use in the value document, the said object is achieved in that pigment cores are given a coating by means of physical vapour deposition (PVD), chemical vapour deposition (CVD) and/or a plasma process and/or a sol-gel process and/or polymerisation and/or electrochemical/galvanic coating and/or eddy coating process and/or by means of self-assembling and/or hybridisation. To ensure that, in order to avoid screening the pigment core from the applied electrical field, the coating of the pigment core surrounds this only partly, the pigment cores are advantageously after coating subjected to a grinding process such that part of the coating is broken away so that then at most one part of the surface of the pigment core concerned is covered with the coating.

The grinding process is suitably performed in a ball mill, where before the start of or during grinding a grinding aid is supplied. Suitable grinding aids in particular are acetylcholine and/or oil and/or a watery suspension.

For a particularly low production cost the grinding process can advantageously be integrated in the ink production. For this the grinding process is advantageously performed on ink production in a three roller ink machine where the coated pigments

are part of the ink. Advantageous further constituents of the ink are ink binders and ink pigments. To ensure the desired comparatively fine-grained structure of the pigments, the spacing of the surfaces of the rollers of the three roller ink machine is advantageously set to a value of maximum the mean diameter of the pigments.

The grinding process in an advantageous embodiment is performed for a maximum of two hours to ensure that the coating is not removed again completely from the pigment cores.

The advantages achieved with the invention comprise in particular a wavelength-selective transmission due to the optically active coating of the pigment cores. This is achieved for example in a monolayer coating by means of a non-linear absorbent coating with targeted doping e.g. with metal ions (Fe^{3+}, Co^{3+}, Ni^{3+}). Furthermore by multilayer coating of the pigment cores in which two, three or more coating layers with fully or partly different refractive indices can be provided, because of interference effects a targeted modification is achieved of the spectrum emitted by the electroluminescent pigment cores. This spectrum can in particular be structured comparatively narrow band so that a particularly characteristic signature of the emission spectrum can be achieved. It is thus possible, by suitable material choice for the electroluminescent pigment core in combination with the specification of suitably selected coating parameters i.e. in particular suitably selected refractive indices and layer thicknesses for the coating layers, to set pigment groups or types distinguishable from each other by their emission spectrum so that with regard to their characteristic emission wavelengths, mutually distinguishable security features can be provided.

Due to the resulting achievable high flexibility in the emission properties in the security features, a particularly high security standard can be achieved in the security document concerned. The possibility of targeted use of properties of pigment coatings is now achieved for a pigment class important for mechanical verification of value and security documents.

In addition in a particularly favourable manner local amplification of the stimulating electrical field can be achieved if the coating at least in one layer has a certain

electrical conductivity. The coating layer concerned then acts namely in the manner of a local "floating" electrode in the immediate physical vicinity of the electroluminescent material, which causes a compression and focussing of the electrical field applied contactless from the outside in the immediate environment of the electroluminescent material. This means that even at comparatively low externally applied field intensities, the excitation field of the electroluminescent material can be exceeded locally so that a reliable excitation of the luminescence is achieved with comparatively low externally applied field intensities. Because of the particularly advantageous combination of these effects therefore a particularly clear narrow band spectrum can be generated even with the relatively low test field intensities used during evaluation.

An embodiment example of the invention is explained in more detail below with reference to a drawing. Here:

Fig. 1 shows a value document in top view,

Fig. 2 shows the marker region of the value document in Fig. 1 in cross section,

Fig. 3 shows sections through the security element of the value document in Fig. 1 (diagrammatically),

Fig. 4,5 show an electroluminescent pigment in cross section,

Fig. 6 shows diagrammatically an emission spectrum of an electroluminescent pigment with uncoated (Fig. 6a) and coated (Fig. 6b-6g) pigments,

Fig. 7 shows examples of electroluminescent pigments in cross section, and

Fig. 8 shows a section through part of a security element during its production (diagrammatically).

The same parts carry the same reference numerals in all figures.

The value document 1 in figure 1 which can for example be a bank note, an identity card, a chip card or any other security document or product secured against counterfeiting or imitation, comprises as a base element a carrier body 2 which depending on application of the value document 1 can be constructed of paper, plastics, laminated plastic layers or other suitably selected material. Applied to the carrier body 2 in the marker region 1 is a security element 6. The security element 6 and the marker region 4 covered by this can be dimensioned and designed according to any criteria tailored to the application and in particular be designed for optical depiction of a printed image for example a numerical value.

The security element 6 serves in the manner of a security feature to identify whether value document 1 is genuine. For this verification or authentication processes are applied which check particular chemical or physical properties of the security feature and thus detect whether the security feature corresponds to expectations.

The security element 6 is specially designed for automated evaluability of its security function. For this the security element 6 as shown in the embodiment example in Fig. 2 in cross section comprises in the marker region 4 a marker layer 8 applied to the carrier body 2. The marker layer 8 is constructed to ensure automated evaluability on the basis of electroluminescent pigments 10. Thus for authentication or analysis of the security element 6, contactless irradiation of electromagnetic radiation into the marker layer 8 by a suitably selected tester is provided, as disclosed for example in DE 197 08 543. The electromagnetic radiation irradiated into the marker layer 8 triggers in the pigments 10 electroluminescence phenomena, where the electromagnetic radiation generated in response can be detected by a suitable sensor and evaluated automatically.

As shown in figure 3, the marker layer 8 can be applied to the carrier body 2 by a printing process, in particular by means of screen printing, rotogravure, offset printing or letterset printing. Here the marker layer 8 comprises firstly the electroluminescent pigments 10 and secondly further constituents of the printing ink, for example ink pigments and/or ink binders 12. As an alternative to the printing process, another coating technique can be used such as for example painting. In the embodiment example according to figure 3 the security element in contrast comprises a substrate

14 and a coating 16. The substrate 14 can be a paper, plastic or laminated material. As a coating 16 in this case a powder comprising the electroluminescent pigments 10 or a mixture of the type shown in figure 3a can be used. The security element 6 with the structure shown in figure 3b can be connected with the value document 1 for example by adhesion or lamination.

In a further embodiment example for the production of security element 6 or the value document 1, a powder comprising the electroluminescent pigments 10 can be mixed with plastics particles or plastics precursor particles and processed into a film by means of calendering, extruding or film casting. The film can itself constitute the value document 1 or the security element 6 or be connected with a carrier by means of one or more lamination or adhesion steps.

The security element 6 is designed to meet particularly high security standards. For this the electroluminescent pigments 10 of the security element 6 have a particularly narrow band emission spectrum in response to the irradiated alternating field so that with suitable tuning of the tester, individualised detection and allocation of a specified group or type of electroluminescent pigments 10 is possible. To guarantee this, the electroluminescent pigments 10 each have a pigment core 20 shown as an example in figure 4 which is delimited by its surface 22. The pigment core 20 comprises an electroluminescent material i.e. a material which emits electromagnetic radiation on application of an electrical alternating field. Typical electroluminescent materials comprise a host lattice, a II-VI compound for example zinc sulphide (Zns), zinc selenide (ZnSe), strontium sulphide (SrS), calcium sulphide (CaS) or cadmium sulphide (CdS). Such materials have an activator, where this activator is provided as doping in the host lattice. Such doping can comprise copper (Cu), gold (Au) or manganese (Mn).

Furthermore electroluminescent materials have co-activators which also constitute doping of the host lattice. This doping can be formed firstly as halogenide ions (chlorine ions (Cl^-), bromine ions (Br^-) or iodine ions (I^-)), or as trivalent cations (aluminium ions (Al^{3+}), gallium Ions (Ga^{3+}), indium Ions (In^{3+}), europium ions (Eu^{3+}), promethium ions (Pm^{3+}), praseodymium ions (Pr^{3+})). A common electroluminescent material comprises for example a zinc sulphide host lattice with a manganese and

chlorine doping (ZnS: Mn, Cl) and preferably has a cubic crystal lattice. Alternatively or additionally the doping can be silver (Ag), iron (Fe), cobalt (Co), nickel (Ni) and/or selected rare earths such as thulium (Tm), terbium (Tb), dysprosium (Dy), gadolinium (Gd), ytterbium (Yb), samarium (Sm), europium (Eu).

The electromagnetic radiation emitted by the electroluminescent pigment 20 on excitation by an electrical alternating field lies in the wavelength range between 200 nm and 3 μm. The mean diameter (the so-called D-index 50 value) of such pigment cores 20 in the embodiment example is maximum 30 μm, preferably less than 25 μm, particularly advantageously around 1 μm to 15 μm.

In order to guarantee the desired optical properties, to form the actual pigments 10 the pigment core 20 concerned is surrounded by an at least monolayer, optically active coating 24. Here for example with a monolayer coating a wavelength-selective transmission takes place by means of non-linear absorbent coating by targeted doping i.e. with metal ions (Fe^{3+}, Co^{3+}, Ni^{3+}). In the embodiment example according to figure 5, to make targeted use also of interference effects, an optically active coating 24 is shown as three layers 26, 28, 30. However another suitably selected number of coating layers is possible, for example two or more than three.

The layers 26, 28, 30 forming this coating 24 are made of an inorganic material in the embodiment example. They can however also be organic materials on a polymer basis e.g. PET and/or PMMA. Suitable inorganic materials are metals, in particular iron (Fe), cobalt (Co), nickel (Ni), chromium (Cr), molybdenum (Mo), tungsten (W), vanadium (V) or niobium (Nb). Metal oxide layers are preferably constructed as silicon dioxide (SiO_2), silicon monoxide (SiO), titanium dioxide (TiO_2), yttrium oxide (Y_2O_3) or zirconium dioxide (ZrO_2). The thickness of such a layer 26, 28, 30 should be maximum 1 μm, preferably however 50 to 200 nm.

The optically active coating 24 is applied to the pigment core concerned with the aim of modifying in a suitable manner the emission spectrum of the electroluminescent material of the pigment core 20 by suitable use of interference, and in particular making this comparatively narrow band. For this layers 26, 28, 30 of coating 24 of the embodiment example are selected such that the refractive index differs

substantially between adjacent layers 26, 28, 30. This guarantees that the electroluminescent material forming the pigment core 20 on excitation by an electrical alternating field emits an electromagnetic radiation which then exposes the coating 24 to interference effects.

The layers 26, 28, 30 in respect to layer thickness and refractive index are structured such that the electromagnetic radiation emitted by the electroluminescent material of the pigment core 20 passes the layers only in specific preset regions of the wavelength spectrum. The following known laws are applied:

$$n \cdot d = m \cdot \frac{\lambda}{2}$$

or

$$n \cdot d = m \cdot \frac{\lambda}{4}$$

depending on whether an amplification or attenuation is to be achieved in the wavelength region concerned, where m is an integer and λ the wavelength of the electromagnetic radiation to be amplified or attenuated. Layers 26, 28, 30 are then indicated as so-called $\lambda/2$ or $\lambda/4$ layers.

The use of such a coating 24 for the pigment cores 20 significantly modifies the emission spectrum of the pigment cores 20 as explained for example with reference to the spectra in figures 6a to 6g. Whereas, as figure 6a shows qualitatively in the form of an intensity(I)-wavelength(λ) spectrum for a non-coated pigment core 20, the electroluminescent material has a comparatively broadband emission spectrum with a maximum at a wavelength of λ_0, the width of this spectrum can be reduced significantly by the coating 24. One example of this is shown in figure 6b in a further intensity(I)-wavelength(λ) spectrum. This spectrum, characteristic of electroluminescent pigments 10 formed from pigment cores 20 with a coating 24, has a far smaller bandwidth $\Delta\lambda$ in comparison with the spectrum shown in figure 6a. In the embodiment examples shown in figures 6b and 6c, the coating 24 is selected such that both for wavelengths below wavelength λ_0 (or λ_0 and λ_1) and for

wavelengths above wavelength λ_0 (or λ_0 and λ_1) a filtering or attenuation of the emitted radiation is performed so that in this case the coating 24 acts in the manner of a band filter and a maximum is achieved (figure 6b), or several maxima e.g. two maxima (figure 6c). Depending on the desired specification for the spectrum of the electroluminescent pigments 10, the coating 24 can also be designed in the manner of an upper edge filter (figure 6d) which attenuates in particular the emitted radiation of a wavelength of more than the wavelength λ_0, or in the manner of a lower edge filter (figure 6e) which attenuates in particular radiation of a wavelength of less than the wavelength λ_0. Furthermore by corresponding presetting an additional maximum (figure 6f) can be generated or a maximum shifted in the emission spectrum as indicated in figure 6g by the double arrow.

In order with the selected materials, in particular with regard to the metallic components in the coating 24, to avoid complete screening of the pigment cores 20 from the applied electrical alternating field as a result of the Faraday effect, in the embodiment examples in figure 7 the coating 24 is applied to the pigment core 20 concerned such that it only partly covers its surface 22. To guarantee this, in production of the value document 1 a process can be applied for which an intermediate product is shown in figure 8. In this embodiment example for production of the security element 6, a substrate 14 is provided for the security element 6. A resin 32 is applied to the substrate 14, the resin 32 being softened by heat transfer after or before or during the application. Pigment cores 20 of an electroluminescent material are then scattered onto the surface of the resin 32. This is preferably done through a sieve so that a particularly even distribution of the pigment cores 20 is guaranteed. The softening of the resin 32 is set to an intensity such that the pigment cores 20 do not sink completely into the resin 32 but almost all cores protrude with part of their surface from the resin 32. Then for example by means of PVD or CVD processes a coating is applied so that the pigment cores 20 are only partly coated.

Alternatively it can also be provided to produce the pigments 10 in a first working step with complete coating 24 as shown in figure 5. The coating of the pigment cores 20 with the coating 24 can then take place in particular by means of physical vapour deposition (PVD), chemical vapour disposition (CVD) or a sol-gel process. Starting

from such prepared pigments 10, in order to guarantee an only partly coated surface 22 of the pigments 20, a grinding process is performed after the coating step. By grinding a part of the coating is broken away from the initially fully coated pigment core 20. The grinding process is performed for example in a ball mill, where before or during grinding a grinding aid is added to the powder. Suitable grinding aids can be acetylcholine ($[N(CH_3)_3(C_2H_50)]^+COO^-$), oil or a watery suspension.

Alternatively the grinding process can take place as part of production of a printing ink so that the overall necessary production complexity is kept particularly low. For this the electroluminescent pigments 10 are added to a printing ink with which the value document 1 can then be printed to produce the security element 6 and its marker layer 8. The ink which is generally composed of a binder and ink pigments in this case contains in addition the electroluminescent pigments 10 with the complete, optically active coating 24. If the ink is now placed in a three roller ink machine as normal in ink production in general, and the spacing between the surfaces of the rollers of the three roller ink machine set such that the spacing is slightly less than or at most corresponds to the mean diameter of the powder particles, then the powder particle cores with their complete coating are subjected to a grinding process so that subsequently a mixture is present of ink and electroluminescent pigments 10, the pigment cores 20 of which are only partly coated on their surface 22.

The grinding time in the ball mill or the grinding process in the three roller ink machine is preferably 30 minutes to 2 hours. After this period a sufficient homogenisation is achieved, where destruction of the pigment core 20 by grinding is safely avoided.

Reference List

1	Security document
2	Carrier body
4	Marker region
6	Security element
8	Marker layer
10	Electroluminescent pigment
12	Arrow
14	Electrodes
16	Coating
20	Pigment core
22	Surface
24	Optically active coating
26,28,30	Layers
32	Resin

I	Intensity
λ, λ_0, λ_1	Wavelength
$\Delta\lambda$	Bandwidth